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The Potential Impact of Acid Precipitation on Wisconsin's Fisheries

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ABSTRACT

Wisconsin's largest concentration of lakes lies in an area geochemically similar to areas in Scandanavia, Ontario and New York. In these areas, hundreds of lakes are now devoid of fish because of acid precipitation. A concern that Wisconsin's fisheries may be damaged by acidity is the reason for this evaluation.

Acid precipitation is currently falling on all of the northern United States east of the Missisippi River. Although there is no evidence that any Wisconsin lakes have been damaged by acid rain, over 2,700 lakes in 21 northern Wisconsin counties have natural pH values less than 6.0. Below pH 6.0, heavy metals become more soluble and toxic to fish, and many fish species begin experiencing reproductive problems. All trophic levels are affected with changes in the species composition of bacteria, algae, zooplankton and benthic populations. Amphibians and piscivorous birds may also be affected.

Acid precipitation originates in the atmosphere as oxides of sulphur and nitrogen are converted to sulphuric and nitric acids. Over 60 percent of the sulphur emissions originate from the combustion of coal by utilities and industry. In the next fifteen years, coal usage is expected to triple.

Reducing the levels of acid precursors will be expensive but the alternative is to pay with the loss of a resource, a source of recreation for thousands of people, and a tourist industry based on trade with anglers. Many state and federal agencies are concerned with the problem but questions in several key areas still remain unanswered.

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INTRODUCTION

When considering the topic of air pollution, one usually thinks of the smoke, and sulfurous smog that covers our major cities. Until recently, it has never been considered that air pollution over Wisconsin's beautiful northern woods and lakes could be causing serious problems. This is not to imply that there is an imminent threat to human health in breathing the air. The danger lies in the possibility that as rain and snow cleanse the air of its pollutants, they become highly acidic and in turn acidify lakes and streams.

The problem is more than hypothetical. In Norway and Sweden, a decline in the fisheries began in the 1920's due to acid fallout (Jensen and Snekvik, 1972). Today over 5,000 lakes are so acidic that they no longer support fish. According to the Canada-United States Research Consultation Group (1979), Ontario has at least 140 lakes which have become acidified. The Ministry of the Environment has proclaimed that at the current rate all fish will disappear from over 40,000 lakes within the next 20 years.

In the United States, the inability of fish to survive in an acid environment was first described by Webster (1961) who noted the loss of all fish except brook trout from a small lake in the Adirondack Mountains. Today the fisheries have been lost from 180 lakes in the Adirondacks (Jones, 1979), and the New York Department of Environmental Conservation (1978) states that as many as 50 percent of the brook trout lakes may be devoid of fish by 1990.

The concern for Wisconsin's waters stems from the fact that our largest concentration of lakes lies in an area geochemically similar to that of Scandanavia, southern Ontario and upper New York State. Data on Wisconsin's rainfall water quality is scanty but Cogbill and Likens (1976) showed that acid rain is falling on nearly all of the United States east of the Mississippi River. In addition, biweekly rainfall samples collected at Boulder Junction in Vilas County, Wisconsin in 1979 (Tablot, personal communication) had pH values from 4.2 to 4.6 -- over 10 times the acid content of normal rainfall. It has been suggested by Arne Henriksen (Likens et al., 1979) that sustained rainfall of pH 4.3 or less is enough to cause severe acidity problems in soft, poorly buffered and naturally acidic lakes such as are common in northern Wisconsin.

As of this writing there is no evidence that any lakes in Wisconsin have been lost to acid rain, but the experiences of Scandanavia, Ontario and New York provide legitimate cause for concern. This paper will define and explore the acid rain phenomenon as it relates to Wisconsin waters, giving special attention to potential impacts on the state's fisheries.

ATMOSPHERIC DEPOSITION

Acidity refers to the hydrogen ion concentration [H+] of a liquid, and is normally expressed in terms of pH units. The pH of a solution refers to the negative logarithm of the hydrogen ion concentration:

$$pH = -\log [H^+]$$

and is expressed on a scale running from pH 1 to pH 14. A pH of 1 is the most acidic and pH 14 is the most alkaline or basic. Pure water is neutral and has a pH of approximately 7. Because the pH scale represents a logarithmic relationship to acidity, each pH unit equals a tenfold increment of hydrogen ions. Therefore a solution of pH 5 is 10 times as acidic as a solution of pH 6, and a solution of pH 4 would be 100 times as acidic as the pH 6 solution.

Natural rainfall is normally weakly acidic because in the atmosphere it becomes saturated with carbon dioxide (CO_2) which is in equilibrium with the bicarbonate ion (HCO_3^-) and carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^=$$

The lower natural limit of rainfall pH is 5.6 and precipitation with values below 5.6 is referred to as acid rain, although acidity can come from rain, snow or dry fallout. The most extreme example of acid rain was reported from Scotland in 1974 where the rainfall pH was 2.4 -- roughly the equivalent of vinegar (Likens et al., 1979).

The precursors of acid rain consist of oxides of sulphur (SO_x) and nitrogen (NO_x) which are converted to sulphuric (H_2SO_4) and nitric (HNO_3) acids. Cogbill and Likens (1974) determined that the acidity in rainfall consists of approximately 65 percent H_2SO_4, 30 percent HNO_3 and less than 5 percent hydrochloric acid (HCl). Acid rain precursors originate primarily from the combustion of fossil fuels such as in electrical power generation, automotive exhaust and industrial emissions. Coal usage is responsible for about two-thirds of the SO_x emissions, while the largest source of NO_x is automobile exhaust. The processes in which the oxides are converted to acids are not clearly understood, but are apparently dependent upon a variety of environmental conditions including temperature, humidity and sunlight.

In 1968, emissions from anthropogenic sources in the United States contributed approximately 33.2 million tons of SO_x and 20.7 million tons of NO_x to the atmosphere (Likens et al., 1972). The average residence time of sulphur in the atmosphere is two to four days, and the conversion rate used by EPA (1979) for SO_2 to $SO_4^=$ is 2 percent per hour during the daytime, and 0.5 percent per hour at night. Therefore, acid can fall hundreds of miles from its original source, and such precipitation may be more acidic than the rainfall in the immediate vicinity of the emission. In the United States, the largest concentration of sulphur emitting sources is in the Ohio River Valley (Fox, 1976) and is being blamed for the acid rain problems in the Adirondacks. Canada's largest point source of SO_2 is a nickle smelting complex in Sudbury, Ontario which emits over 2.4 million metric tons of SO_2 per year (Schofield, 1976).

Wisconsin has only recently recognized the excessive acidity of its rainfall and as yet has not identified the source of the pollution. Although speculations point to all adjacent major metropolitan areas and to industrial centers as far away as the Ohio River Valley, the exact origin of the acidity cannot be identified without better data.

Acid loading to a given locality is fairly consistent from year to year, but the acidity of individual rainstorms will vary with environmental factors such as wind speed and direction, and rainfall amounts. Seasonal variations also occur, and summertime values are commonly more acidic than those during the winter (Likens et al., 1972). Hornbeck et al. (1977) recognize such differences and suggest that snow may be less efficient than rain at removing sulphur compounds. Although snowfall may be less acidic than summer rains, it presents a greater danger because of the accumulations of acid in the snowpack. In Norway, Overrein (1976) found that snowfall over an eight day period in 1974 contributed 850 kg sulphate per km^2, 90 percent of which was sulfuric acid. Further measurements of spring run-off found pH's plunging as low as 3.0. Oden (1976) describes how, in the first phase of snowmelt, the major ions separate from the snowpack producing meltwater which is salty and much more acidic than the bulk of the snow. It normally drains on top or in the upper layers of the soil until reaching a stream where it can have major impact on the acidification of the stream, especially those in smaller watersheds. The initial rapid pH drops can be especially harmful to fish eggs and larvae. The remaining snowpack is relatively pure and will rapidly restore the pH.

Hultberg (1977) explains how a similar process affects lakes. He reports a pH drop on Lake Stensjon, Sweden from a normal pH of 5.0 to 3.4 at the ice-water interface and from 5.0 to 3.8 at a depth of one meter. The pH drop was noticeable to a depth of 5.0 meters near shore because of incoming acid run-off, but only to 3.0 meters in the center of the lake. After the ice had gone out, the lake returned to its normal pH level. Hultberg suggests that it may not be only the decline in pH which harms fish, but also the consequential increase in pH.

GEOCHEMICAL INFLUENCES

Just as CO_2 saturated water acts as a weak acid, it also can act as a weak base as the bicarbonate ion absorbs excess hydrogen ions to yield CO_2 and water:

$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2$$

The bicarbonate ion, as a buffer, has a maximum reactiveness at pH 6.3 and a minimum at pH 5.5. As acidity increases, more bicarbonate is converted to CO_2 until pH 4.6 where all carbonates and bicarbonates are in the form of CO_2.

Lakes lying on limestone bedrock ($CaCO_3$) are rich in bicarbonate ion because the limestone exposed to carbonic acid will readily dissolve to form soluble calcium bicarbonate:

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca(HCO_3)_2$$

Many lakes in the southern half of Wisconsin lie on dolomitic and limestone bedrock and the waters are, consequently, hard, alkaline and well buffered (total alkalinity > 150 ppm $CaCO_3$). In northern Wisconsin, most of the lakes lie on sand, sandstone, insoluble rocks or on precambrian granite, none of which are inducive to high alkalinities. In addition, the reducing environment of the northern bog areas produces humic and tannic acids which can further increase the acidity of surface waters. Therefore, most northern Wisconsin lakes are very soft and slightly acidic. Figure 1 shows that over 2,700 lakes in counties on the Precambrian Shield have a pH value less than 6.0. Nearly all are small seepage lakes and are naturally acidic.

Natural waters are typically buffered by soluble substances such as: phosphates, organic acids and amino acids; colloidal matter including humus and seston; and bicarbonate. The addition of anions such as sulphate from acid rain replaces carbonates to further inactivate the bicarbonate system. While diagrammatic, Figure 2 demonstrates the importance of bicarbonate as a buffer to soft water lakes. It can be observed that in lowering the pH from 6.7 to 6.3 a large portion of the buffering capacity is lost (about 30%). Below pH 6.0 very small amounts of additional acid can cause substantial reductions and fluctuations of pH. As Oden (1976) points out, at pH 5.5, the $SO_4^=/HCO_3^-$ ratio is zero, and virtually all of the buffering capacity is lost. Such findings agree with those of Wright and Gjessing (1976), and Galloway et al. (1976).

An additional problem complicating the acid rain issue is that of increasing solubility and toxicity of metals at low pH levels. Copper, zinc, cadmium and lead have been found in substantial quantities in acid rainwater (Wright et al., 1976), and Hagen and Langeland (1973) have found large quantities of zinc and lead together in acid snow and meltwater. Acid snowmelt can mobilize aluminum from topsoil in quantities large enough to kill fish (Schofield, 1976), and as the International Joint Commission (1979) points out, acidity can cause toxic metals such as mercury, copper, lead, nickle, aluminum and zinc to be released from lake sediments as well as from topsoil. Schindler et al. (1980) demonstrated that aluminum, manganese, iron and zinc are released from sediments at pH 5.0 and 6.0, and zinc was released at levels which have been shown to be toxic to fish.

EFFECTS ON FISHES

For the sake of prediction, it would be convenient if there was a single pH value which was a critical minimum for fish populations, but there is none. The European Inland Fisheries Advisory Commission (1969) states that "there is no pH range within which a fishery is unharmed and outside which it is damaged, but rather there is a gradual deterioration as pH values are removed from the normal range." The degradation of fish populations is usually more the result of all secondary effects related to pH and acid rain, than to the hyperacidity itself. In laboratory situations, fish have been acclimated to pH values as low as 3.7, but most populations will begin to decline as the pH approaches 5.0. A recent survey on lakes in the Adirondacks, over 610 meters in elevation with pH less than 5.0, found that 90 percent had no fish (Schofield, 1976). Surveys on similar lakes in 1929-1937 found only 4 percent without fish.

Calculations of the approximate values at which fish in the La Cloche Mountain Lakes of Ontario stopped reproducing are shown in Table 1 (Beamish, 1976). Walleye and smallmouth bass are apparently more acid sensitive than lake trout while perch are fairly tolerant. These data apply to a specific set of environmental conditions however, and do not take into account factors such as altered heavy metal concentrations or pH fluctuations from spring meltwater. For northern Wisconsin, it is difficult to predict which species of

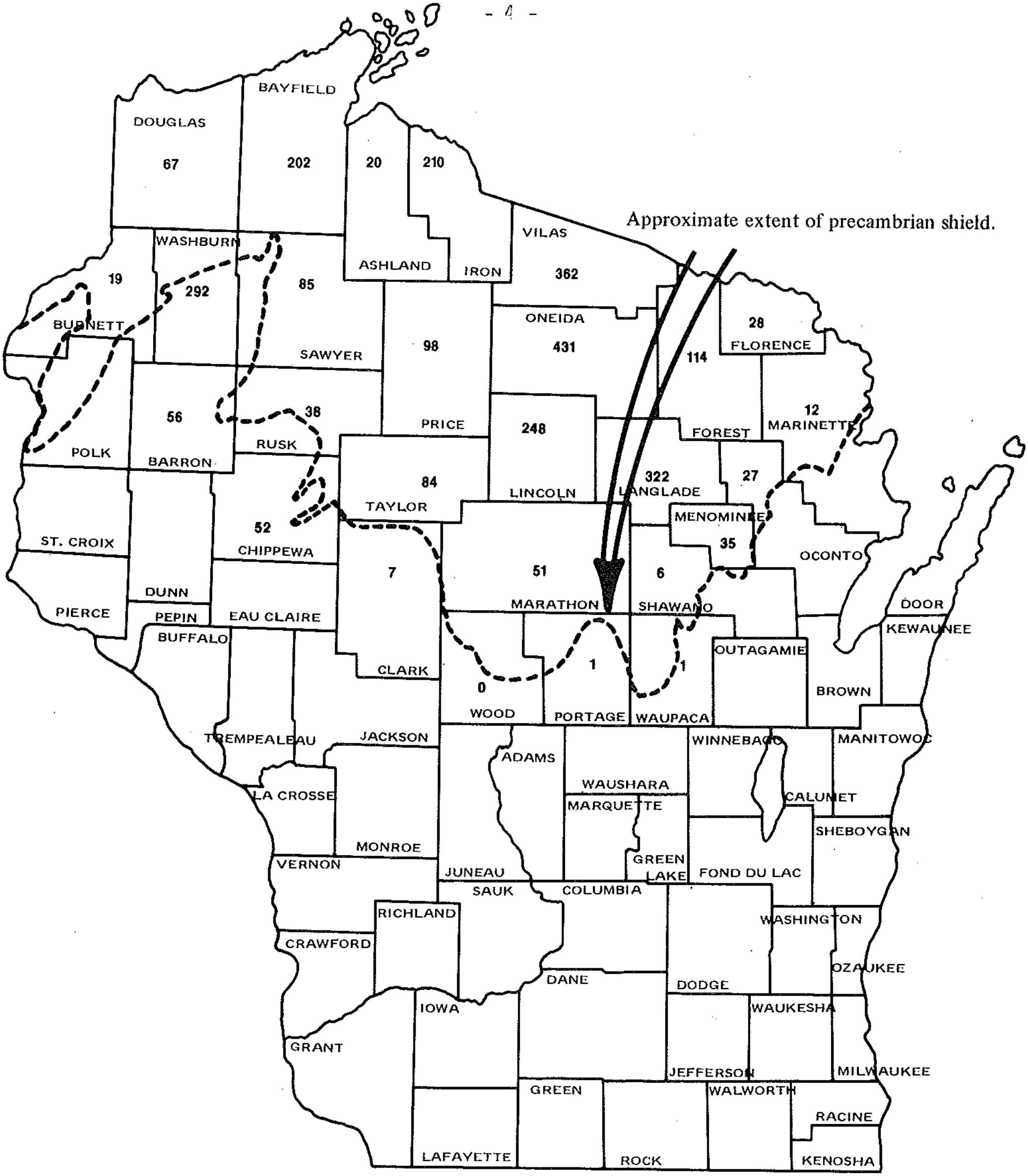

FIGURE 1. Number of lakes with pH less than 6.0 in each county.
From DNR Fish Mgt. Surface Water Resource Inventories.

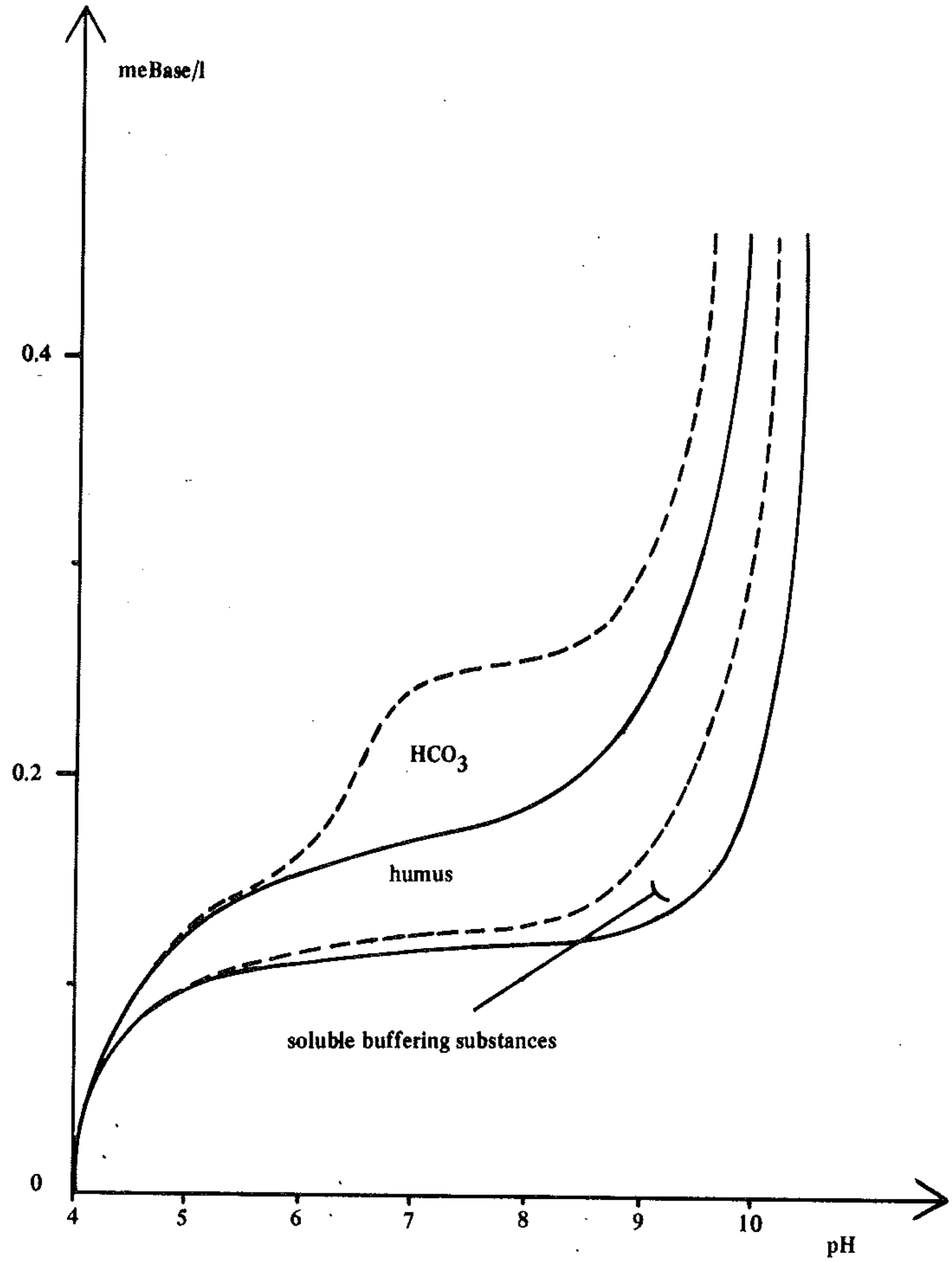

FIGURE 2. Total buffering capacity of surface water. From Oden (1976).

fish may be the most sensitive to environmental acidification because the species composition of the most acidic lakes is different than that of the more buffered lakes. Nearly all of the lakes with pH less than 5.5 are seepage lakes under 60 acres in size, and currently support populations of slow-growing bluegills, perch and largemouth bass. Some lakes with pH values of approximately 5.0 will support a few muskellunge. Northern Wisconsin's larger lakes are generally drainage lakes with higher alkalinities and are therefore more productive than the seepage lakes. They therefore are capable of supporting a more diverse fishery which usually includes walleye and smallmouth bass. Current fish distribution is therefore more a function of lake size and habitat than of pH, and the more acid sensitive species are apparently found in the more buffered lakes.

Table 1. Approximate pH at which fish in the La Cloche Mountain Lakes, Ontario, stopped reproduction (after Beamish, 1976).

pH	Species
6.0+ to 5.5	Smallmouth bass *Micropterus dolomieui*
	Walleye *Stizostedion vitreum*
	Burbot *Lota lota*
5.5 to 5.2	Lake trout *Salvelinus namaycush*
	Troutperch *Percopsis omiscomaycus*
5.2 to 4.7	Brown bullhead *Ictalurus nebulosus*
	White sucker *Catostomus commersoni*
	Rock bass *Ambloplites rupestris*
4.7 to 4.5	Lake herring *Coregonus artedii*
	Yellow perch *Perca flavescens*
	Lake chub *Couesius plumbeus*

Massive fish kills associated with acid rain are the exception rather than the rule. The loss of Norway's salmon and trout fisheries was a gradual process beginning in the 1920's, however in December 1948, over 200 dead salmon and trout were picked up from the Frafjord River. The pH levels at the time were between 3.9 and 4.2 (Jensen and Snekvik, 1972). Other fish kills have occurred when toxic metals such as aluminum or zinc have been in combination with high acidity. In such cases, ruptured gill filaments or gill necrosis is the apparent cause of death. Because of these gill problems, winterkill may become more prevalent as acid-stressed fish are often more susceptible to low dissolved oxygen.

The most common effect of hyperacidity on fish is manifested as poor recruitment from natural reproduction. This results from failures in fertilizing and hatching eggs and spawning failures of the females. In addition the smaller fish, especially larvae, are more sensitive to acidity than larger fish.

Carrick (1979) found that the fertilization and hatchability of the eggs of Atlantic salmon (*Salmo salar*) and brown trout (*Salmo trutta*) were not noticeably affected at pH 4.5, but at pH 3.5 all eggs were dead within 10 days. There is some evidence that certain genetic strains of a species are more acid resistant, and that some fish and eggs can be conditioned to be acid tolerant. Acclimation to acidity apparently plays a part as brook trout eggs incubated at a low, but sub-lethal pH are less likely to experience acid-induced mortalities upon emergence than eggs incubated in normal spring upwelling (Trojnar, 1977).

As the pH dropped from 5.0 to 4.5 in Lumsden Lake, Ontario, Beamish (1974) found that white suckers (Catostomus commersoni) exhibited spinal deformities, a failure to spawn, and slow growth in spite of adequate food supplies. Further studies (Beamish et al., 1975) found that the females failing to reproduce also exhibit low serum calcium levels. Packer and Dunson (1970) report that at pH 3.5 brook trout lose 50 percent of their total body sodium to the water, and it may be that calcium regulation is interferred with in a similar manner. Low serum calcium levels can apparently cause spinal deformities, and result in poor food utilization. Thus, the females fail to release their eggs, and adsorb them back through the circulatory system.

In an acid environment, all trophic levels are affected. Bacterial decomposition is inhibited, which results in increased organic accumulations and a decrease in nutrient cycling. Fewer nutrients and low alkalinities at high acidity levels further reduces primary productivity, which ultimately reduces fish production.

Many algae species are also intolerant of low pH levels. Most green algae and diatom species disappear below pH 5.8, and among the zooplankton, most daphnians disappear below pH 6.0 (Almer et al., 1974). In the benthic community, very few Gammarus are found below pH 6.0, and most insects disappear below pH 5.7 (Wright et al., 1976). The influx of acid meltwater and the resultant fluctuations in pH may be particularly damaging to small streams. Those insects which emerge in late winter and early spring may be especially susceptible.

Macrophyte communities in acid lakes lose diversity and productivity and are characterized in Europe by an increasing dominance of the acidiphile Sphagnum. Large mats of Sphagnum provide a poor substrate for insect fauna and absorb calcium and phosphorus thereby reducing nutrient cycling. Gorham (1978) reports that in North America, acid lake bottoms may be covered with mats of Drepanocladius or Leptodictyum, and suggests that these be investigated in the same context as Sphagnum. Drepanocladius presently grows on the bottom of Crystal Lake in Vilas County, Wisconsin.

Vertebrates other than fish are likely to be affected by acid precipitation. The shallow temporary pools which are breeding areas for amphibians are especially susceptible and it has been shown that spotted salamanders suffer high mortalities due to embryonic malformations at pH levels less than 7.0 (Pough, 1976). Three amphibians on the state's threatened species list are found in the northern part of the state. Included are the spotted salamander (Ambystoma maculatum), Tremblay's salamander (A. tremblayi) and the pickerel frog (Rana palustris).

In the event that fish are lost to acid rain, a corresponding loss could fall to fish-eating birds and mammals. Mergansers and loons feed nearly exclusively on fish, and bald eagles have been found to rely on fish for as much as 90 percent of their diet (Dunstan and Harper, 1975).

THE CONCERN FOR WISCONSIN

Wisconsin's largest concentration of lakes lies in the northern part of the state over a bedrock formation of Precambrian granite. Much of this geologic province is poorly drained and is covered with glacial till which is peppered with small seepage lakes. Top-soils are shallow and lowland vegetation consists of plants such as tamarack, black spruce, leather leaf, sphagnum moss and pitcher plants -- all of which encourage acid or dystrophic conditions in lakes. Other lakes while not dystrophic, are extremely oligotrophic due to a paucity of soluble minerals such as carbonates in their watersheds. Oligotrophic acid lakes are crystal clear and very beautiful, but are nonproductive from a fisheries standpoint. Nevertheless they do provide some fishing, and deserve protection in their present state. Half of all the lakes on the Precambrian shield in Wisconsin, have pH values less than 7.0. As Figure 1 shows, over 2,700 lakes have pH values less than 6.0.

In accordance with EPA water quality standards (Thurston et al., 1979), and findings of other investigators, a pH of 6.0 is a critical minimum for maintenance of a well balanced fishery.

Beamish (1976) showed, that walleye and smallmouth bass may encounter reproductive problems at pH values between 6.0 and 5.5, and as Oden (1976) pointed out, at pH 5.5 nearly all of the bicarbonate buffering is lost thereby allowing further acidification to occur more rapidly. At pH less than 5.0, bacterial decomposition is reduced, many species of algae and zooplankton cannot survive, and the fishery of most Wisconsin lakes is restricted to small bluegills, perch and largemouth bass. Very low nutrient levels and low alkalinities keep biological productivity at a minimum. In fluvial systems, brook trout are probably one of the fish species most tolerant of acid water, but the rapid pH fluctuations caused by acid snowmelt is harmful to all stages of trout development, especially eggs and larvae. Drops in pH down to 5.0 have been known to kill trout within 24 hours (Webster, personal communication).

In summary, over 2,700 small seepage lakes with fairly nonproductive fisheries are in danger of being acidified but the level of danger remains to be determined. At the same time, the trout streams and larger drainage lakes which provide virtually all of the fishing are being threatened by the potential damage of incoming acid snowmelt at spawning time. The potential problem of metals toxicity remains to be investigated.

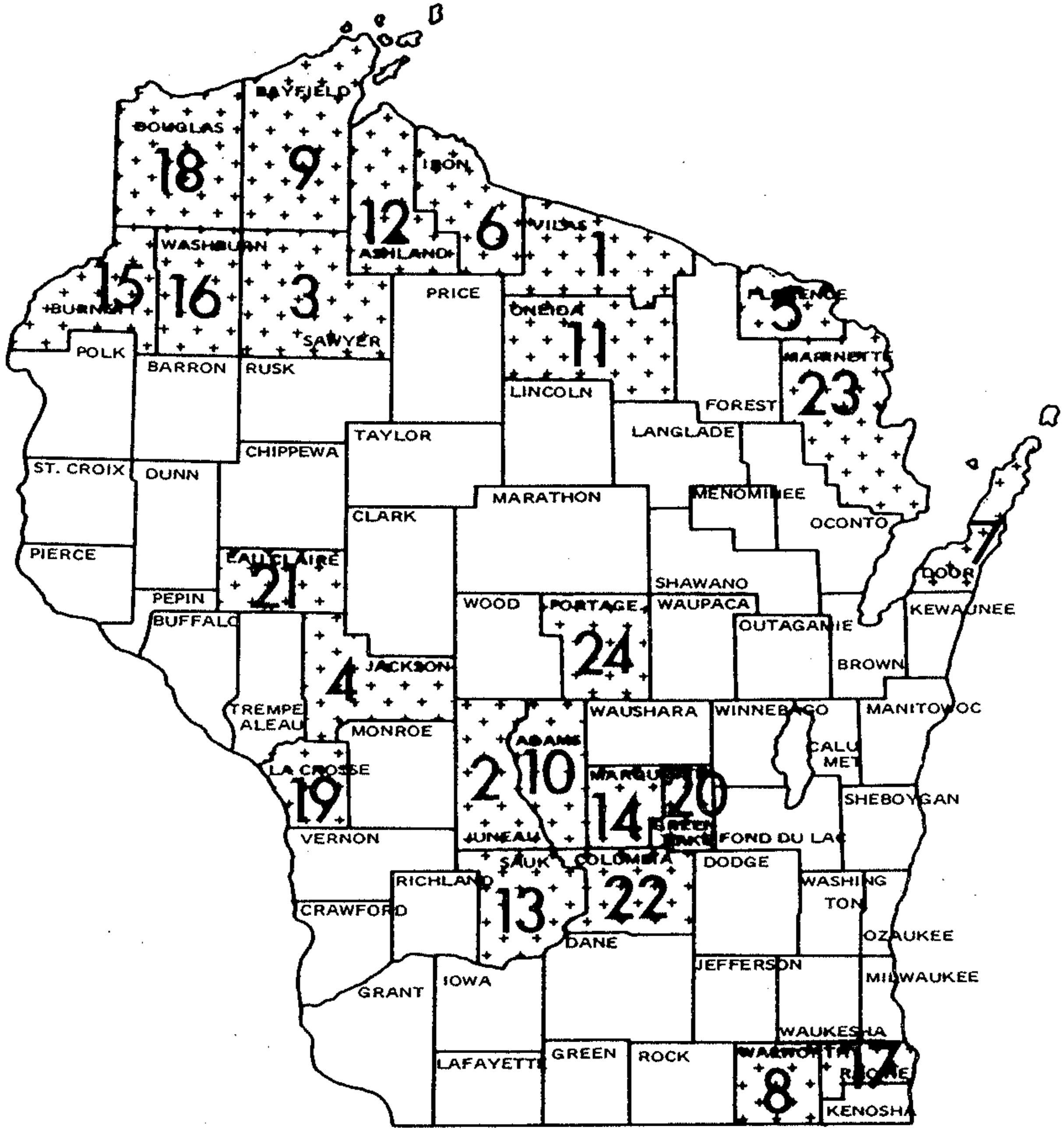

FIGURE 3. Ranking of counties by impact of hospitality-recreation-tourism sales on local economy, 1978.
From Gray et. al., (1979).

No one questions the value of maintaining lake and stream water quality at levels suitable for fish production, but the state's fisheries also have a commercial value to a large and growing tourist industry. Fishing provides outdoor recreation for thousands as well as an important economic base. In 1975, anglers spent 30.4 million days enjoying their sport and at the same time contributed approximately $293 million to the state's economy (Wisconsin Department of Natural Resources, 1979). In 1978, sales from Wisconsin's hospitality-recreation-tourism industry netted nearly $5 billion. Figure 3 shows 11 of the top counties whose local economies are most dependent on tourism, all are in the northern one-third of the state. Therefore the decline of fishing in northern Wisconsin could result in a corresponding loss of revenue to fishing related activities such as motel, restaurant and resort businesses and have a major impact on the local economies.

WHAT IS BEING DONE

Coal combustion by utilities and industry accounts for over 60 percent of the sulphur emissions in the United States. Coal is a major portion of the United States' energy reserve and in the light of the controversy surrounding nuclear power, and our attempts to decrease demands on foreign oil, it is being mined and used at an ever increasing rate. Coal use is expected to triple in the next fifteen years.

In the past, one solution to local air quality problems was to build taller smokestacks thereby attaining "no effect" levels. Although this alleviated local pollution problems, it scattered pollutants high in the atmosphere and created regional problems -- namely acid rain. This air pollution phenomenon is therefore no longer a local or state problem, but one needing national and international attention.

Canada has labeled acid rain as its number one environmental problem, and negotiations are underway to establish a treaty between the United States and Canada to control acid rain precursors.

Although technologically feasible, reducing sulfur emissions will be costly, and will probably be paid for with higher utility bills. The alternative is to pay with the loss of a natural resource and a source of recreation for thousands. Estimates for reducing sulfur emissions by 50 percent are between $5 billion and $7 billion for the northeastern United States and about $350 million for eastern Canada (Urquhart, 1979). Using low sulfur coal is one alternative but it is in shorter supply and is more expensive.

Many new coal fired plants are employing the use of electrostatic precipitators and "scrubbers" to reduce their emissions of suspended solids and SO_x, however older plants are not required to use such devices. Possible experimental techniques include the use of conversion processes such as gasification and liquification, and chemically removing the sulfur prior to combustion.

While new sulfur reducing technologies are being developed, acid rain continues to fall on a wider area of the country, and more lakes are being lost. In the interim, techniques are evolving to treat the effects of the problem. Initial results look promising for breeding acid tolerant strains of brook trout (Webster, personal communication). Lakes are also being treated with lime to decrease their acidity using alkalization techniques developed by Hasler et al. (1951). In New York, the Bureau of Fisheries has limed 52 ponds since 1959 (New York Department of Environmental Conservation, 1978), and two Ontario lakes near Sudbury have also been treated (Scheider et al., 1975). Success rates have been variable and temporary, and the procedure is economically feasible only on small lakes with low flushing rates.

On the national front, President Carter has initiated a 10 year program to study acid rain and its effects, with a first year budget of $10 million. Federal agencies currently involved are the Environmental Protection Agency, Departments of Energy, Agriculture and Interior, the National Science Foundation and others.

In Wisconsin, acid rain is being monitored closely by the EPA-Duluth and the Department of Natural Resources. Other agencies involved are Nicolet College, the University of Wisconsin-Madison, U.W. Extension, the Public Service Commission, and the U.S. Geological Survey.

THE NEED FOR RESEARCH

Background data for acid rain studies in Wisconsin is decidedly lacking. There have been very few analyses of Wisconsin's rainfall water quality, and airshed analyses need to be completed with respect to possible pollution sources. Buffering capacities of northern Wisconsin watersheds remain to be determined, and baseline fish distribution surveys need to be conducted in the state's most acid-sensitive waters. Work has already begun in some of the above areas but there is still much to do. The incorporation of such data is necessary in establishing power plant siting criteria and in making or changing future policies regarding air quality standards.

Wisdom has been defined as the ability to learn from the experiences of others. It is hoped that the experiences of New York, Ontario and Scandanavia will not be taken lightly and that Wisconsin will recognize the potential threat of acid rain before enduring the loss of any fishery resources.

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